

- (21) Application No. 46003/76 (22) Filed 4 Nov. 1976 (19)
(31) Convention Application No. 50/131425 (32) Filed 4 Nov. 1975 in
(33) Japan (JP)
(44) Complete Specification Published 11 Jun. 1980
(51) INT. CL.³ C25D 13/08
(52) Index at Acceptance
C7B 114 304 306 310 316 620 621 650
651 DM
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(54) METHOD OF COATING
STEEL SHEET BY ELECTRODEPOSITION

(71) We, TOYO KOHAN CO, LTD. a body corporate organised under Japanese law of 4-3, Kasumigaseki 1-chome, Chiyoda-Ku, Tokyo, Japan do hereby declare the invention for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:-

5 This invention is concerned with a method of coating steel sheets by electrodeposition wherein the steel sheet is electrolytically treated in a suspension solution and then cured by heat treatment.

Some commonly used methods of producing a coated metal sheet, mainly using polymer resins, are as follows:

10 (1) By roller coating, knife coating, spray coating or immersion coating, an organic solvent-type paint is coated on the metal sheet and then cured by heat treatment.

15 (2) By the same method, a mixture of polymer resin powder and adhesive solution is coated on the steel sheet, and then cured by heat treatment.

(3) By injection coating, a polymer resin powder is coated on the metal sheet.

20 (4) By electrophoretic coating, the metal sheet is coated with an organic solvent containing a polymer resin powder, dried and then cured by heat treatment.

25 (5) By electrophoretic coating, the metal sheet is coated with a treatment solution containing a water-dispersible polymer resin and then cured by heat treatment.

(6) By electrostatic coating, a polymer resin powder is coated on the metal sheet, and then cured by heat treatment.

In methods (1), (2) and (3), it is difficult to control the thickness or uniformity of the coating. Uniformity of the coating thickness with regard to quality control is often one of the most troubling factors. Also, for the application of a thin coating, the said methods are very unattractive from an economical standpoint. Further, when powders containing polymer resin and an inorganic compound are used as coating materials, these methods become more and more difficult.

In the case of methods (1), (2) and (4), where an organic solvent is used, there is often a pollution problem.

30 The method (5) requires that a strong ionic charge be produced by dissociation of the polymer resin. Therefore, the polymer resin used must be carefully chosen. For example, insoluble nylon and polyethylene cannot be electrodeposited by the method of (5).

35 The method (6) has the weakness that adhesion of the resin powder is poor and the coated powder is often easily separated from the base metal sheet by a slight impact or contact after production. In cases where the coating contains metal powder, the coating adhesion deteriorates further.

40 On the other hand, according to Japanese patent publication No. Sho 50-75623, a metal sheet is cathodically electrotreated in a suspension solution containing an alumina sol of 1 to 500 mμ (particle diameter) with a positive electric charge and an organic polymer resin. By use of this method, one can easily control the coating thickness by the amount of electricity used. It is not necessary to use harmful organic solvents; therefore, a public hazard is not

caused by the treatment solution. Also, insoluble nylon and polyethylene and inorganic powder can easily be electrodeposited from the suspension solution as described above.

We have now been able to achieve an improvement in the adhesion of the coating to the sheet over that which has been hitherto achieved.

5 According to the invention therefore there is provided a method of producing a 5 composite coated steel sheet which comprises electrolytically treating a steel sheet in a suspension solution containing a water-soluble or water-dispersible organic polymer resin, at least one water-dispersible sol of a metal compound and at least one infusible organic polymer resin powder, and curing the so treated sheet by heat treatment.

10 Steel sheets coated by the method according to the invention possess excellent corrosion 10 resistance because of the uniform coating with composite materials.

The water-soluble or water-dispersible organic polymer resin which is one of the main components according to the present invention has the effect of improving the coating adhesion. These resins may include the following: phenolic resins, alkyd resins, 15 water-soluble or dispersible acrylic (including polyacrylamide) resins and butadiene resins. 15 The particle diameter of these resins is preferably under 1μ . A particle diameter of more than 1μ is unfavourable because it worsens the appearance of the deposit surface. A concentration preferably in the range of 2 to 50 g/l (as solid) is suitable for improving the coating adhesion. A concentration of less than 2 g/l has little effect on improving the coating 20 adhesion and conversely, a concentration of more than 50 g/l adversely affects the throwing 20 power.

The water-dispersible sol of a metal compound present in the suspension solution may for example be a compound (e.g. oxide or hydroxide) of a metal such as zinc, tin, chromium, 25 nickel, titanium, zirconium or aluminum. The diameter of the sol particles is preferably 1 to 25 500 $m\mu$. A concentration of the above-mentioned sol in the range of 1 to 100 g/l is preferable for the present invention. The treatment solution may contain one or more of these agents. In the case of a concentration of less than 1 g/l, the above-mentioned effects cannot generally be expected. At a concentration of more than 100 g/l, the improvement in film-forming is not in proportion to the increased concentration. On the contrary, it is 30 generally unfavorable because the viscosity of the suspension solution tends to be high, the 30 solution is unstable and causes process difficulties.

Almost any infusible powder of an organic polymer resin can be used for the suspension solution of the present invention, but it is generally required that the powder should not react significantly in the electrolytic solution.

35 For example, there may be used nylon, polyethylene, polypropylene, polyamides, diacryl 35 phthalate, ethylene-vinyl acetate copolymer resins, cellulose acetate butylate, polyurethanes, polystyrene, polycarbonates, chlorovinyl resins, polyfluorovinyl resins, epoxy resins and infusible acrylic resins. The treatment solution can contain one or more of these powder resins. The powder size tends to influence the appearance of the coating layer 40 and coating adhesion. Small size powder forms a dense deposit layer, whereas large size 40 powder makes for a porous deposit layer and poor coating adhesion. But these defects are improved by the treatment with a rolling press after electrodeposition or heat treatment. Therefore, although the powder size is not specifically restricted, it is desirable that it be 45 under 200μ in order to facilitate the production of a satisfactory coating.

45 The concentration of powder in the treatment solution depends on the powder size, the 45 kind of powder and the combination of materials. When the concentration is above 100 g/l, some powders do not have adverse effects on the operation.

A concentration of less than 3 g/l tends to decrease the current efficiency.

50 For the purpose of further improving corrosion resistance, at least one powder selected 50 from a metal, an alloy and a sparingly water-soluble or water-insoluble compound of the said metal are added to the above-mentioned solution.

These powders may include metals such as aluminum, zinc, chromium, cobalt, nickel, iron, tin, lead, copper, manganese, titanium, molybdenum, zirconium, bismuth, antimony and tungsten. Alloy powders include the alloys of said metals. Sparingly water-soluble or 55 water-insoluble compounds include the hydrides, sulfides, chlorides, oxides, sulfates, 55 nitrates, hydroxides and carbides of said metals. One or more of these powders may be used. The preferred size (diameter) of the powder is under 200μ . A diameter of more than 200μ generally gives bad results such as decrease in the formation and effect of the porous coating layer and deterioration of the corrosion resistance.

60 The concentration of inorganic powder depends on the powder size, the kind of powder 60 and the combination of materials, the same as described in the case of the polymer resin powder. Even at a concentration above 100 g/l, some powders do not produce adverse effects in operation.

65 At a concentration of less than 3 g/l, an improved corrosion resistance cannot generally 65 be expected.

A temperature of 10-70°C is suitable for treating with the suspension solution. At a temperature of more than 70°C, it is difficult to keep the concentration of the bath constant because of high evaporation rates.

The current density is not especially critical, but in general the higher densities give greater coating thicknesses.

On electrodeposition of the composite coating, the polarity of the metal sheet treated depends upon the composition of the suspension solution. In general, when the pH of the treatment solution is on the acid side, the metal is cathodically treated. On the other hand, when the pH of the solution is on the alkaline side, the metal sheet is anodically treated.

Agitation during electrotreatment has a tendency to decrease the deposition efficiency, but some agitation may be required in order to uniformly maintain the powder in the suspension solution.

Surface active agents or alcohol may also be added to the treatment medium in order to uniformly disperse the powder in the treatment solution. For example, nylon powder (diameter: 50 μ) can uniformly and quickly be mixed by the addition of 1 g/l of an alkyl betaine-type surface active agent.

After preparing the suspension solution by the above-mentioned method, the metal sheet is cathodically or anodically treated in said suspension solution.

The electrodeposited layer formed on the metal sheet can be rinsed with water and then dried.

The coated metal sheet formed by the above-mentioned method is cured by heat treatment. The conditions of the heat treatment depend on the kind of powder and coating thickness. As a general guide, it is required that the resin powder be in a molten state. Also, before or after curing, a pressure rolling treatment remarkably improves the appearance of the coated sheet.

The present invention is suitable for the surface treatment of various different types of steel sheet. For example, the sheet may be one which has been subjected to a chromic electrotreatment (in a CrO₃/H₂SO₄ bath) or steel plated with chromium, tin, zinc, nickel or aluminum or an alloy thereof or other metals. Also, the method is applicable to steel sheets which have been subjected to a post treatment such as with a chromate or phosphate.

The invention is illustrated by the following examples.

Example 1

A low carbon steel sheet of 0.5 mm thickness, after annealing and temper rolling, was cleaned in 70 g/l of sodium hydroxide solution at a temperature of 70°C for 10 seconds, rinsed with water and then placed in 70 g/l of sulfuric acid for 5 seconds at 20°C and again rinsed with water. The pre-treated steel sheet was immediately treated by the method of the present invention.

Treatment of the present invention:

Bath composition		
chromium hydroxide sol	(average diameter of particles: 100 m μ)	
	35 g/l	
epoxy resin powder (average diameter: 40 μ)	10 g/l	
polyacrylamide (water-soluble resin)	10 g/l	
Temperature	20°C	
Current density (cathodic treatment)	5 A/dm ²	
coating time	15 seconds	

The coated metal sheet formed was blue. The said coated sheet was heated for 2 minutes at a temperature of 250°C and a light blue coated steel sheet of 14 μ thickness was obtained. An Erichsen test indicated an 8 mm depth. The coated sheet showed no evidence of adhesion loss of the coated layer. Also, the corrosion test (salt spray test) provided by JIS (Japanese Industrial Standard) Z 2371 was applied to said coated sheet and the coated sheet did not show any red rust after 200 hours.

On the other hand, in the case where polyacrylamide was not added, red rust was observed after 200 hours in the salt spray test. A steel sheet coated with epoxy powder by

the conventional method of spray coating made interface adhesion worse between the powder and the base metal and the powder was separated from the base metal by a slight impact. The epoxy powder was baked carefully so as to not separate from the base metal. The coated sheet obtained showed red rust after 10 hours.

Example II

The same low carbon steel sheet was subjected to the same pre-treatment described in Example I. After that, the said pre-treated sheet was immediately treated by the method of the present invention.

Treatment of the present invention:

15	Bath composition chromium hydroxide sol	(average diameter of particles:100 mμ) 35 g/l	15
	epoxy resin powder (average diameter:40 μ) polyacrylamide (water-soluble resin)	10 g/l 10 g/l	20
20	zinc powder (diameter:100μ)	100 g/l	
	Temperature	20°C	
25	Current density (cathodic treatment)	5 A/dm ²	25
	Coating time	15 seconds	

The coated sheet formed was gray. The said coated sheet was heated for 2 minutes at a temperature of 250°C and a gray coated sheet of 14μ thickness was obtained.

The Erichsen test showed an 8 mm depth and the coated sheet showed no evidence of adhesion loss of the coating layer. Also, the coated sheet was evaluated by the salt spray test as described in Example I. The results show that no red rust was observed after 500 hours and the addition of zinc powder was effective for improving the properties described above.

On the other hand, the steel sheet coated with epoxy powder only by the conventional method of spray coating had inferior interface adhesion between the powder and base metal. The epoxy powder was baked carefully so as not to separate from the base steel. The coated sheet obtained showed a red rust after 24 hours.

WHAT WE CLAIM IS:

1. A method of producing a composite coated steel sheet which comprises electrolytically treating a steel sheet in a suspension solution containing a water-soluble or water-dispersible organic polymer resin, at least one water-dispersible sol of a metal compound and at least one infusible organic polymer resin powder, and curing the so treated sheet by heat treatment.

2. A method as claimed in claim 1 wherein the water-soluble or water-dispersible organic polymer resin is a phenolic resin, an alkyd resin, an acrylic resin or a butadiene resin.

3. A method as claimed in claim 1 or claim 2 wherein the water-soluble or water-dispersible organic polymer resin is present in the suspension solution in an amount of from 2 to 50 g/l.

4. A method as claimed in any of the preceding claims wherein the infusible organic polymer resin powder is selected from nylon, polyethylene, polypropylene, polyamides, diacrylphthalate, ethylene-vinyl acetate copolymer resins, cellulose acetate butylate, polyurethanes, polystyrene, polycarbonates, chlorovinyl resins, polyfluorovinyl resins, epoxy resins or acrylic resins, which resins have an average particle diameter of under 200μ.

5. A method as claimed in any one of the preceding claims wherein the metal compound of the sol is an oxide or hydroxide of of nickel, titanium, zirconium, chromium, zinc, aluminum or tin having an average particle diameter of 1 to 500mμ.

6. A method as claimed in any one of the preceding claims wherein the sol is present in the suspension solution in an amount of from 1 to 100 g/l.

7. A method as claimed in any of the preceding claims wherein the suspension solution also contains at least one powder selected from a metal, an alloy and a sparingly water-soluble or water-insoluble metal compound.

8. A method as claimed in claim 7 wherein the metal powder is an aluminum, zinc, chromium, cobalt, nickel, iron, tin, lead, copper, manganese, titanium, molybdenum, zirconium, bismuth, antimony or tungsten powder having an average particle diameter of under 200 μ .
- 5 9. A method as claimed in claim 7 wherein the alloy powder is selected from alloys of the metals of aluminum, zinc, chromium, cobalt, nickel, iron, tin, lead, copper, manganese, titanium, molybdenum, zirconium, bismuth, antimony or tungsten, which alloy powder has an average particle diameter of under 200 μ . 5
- 10 10. A method as claimed in claim 7 wherein the sparingly water-soluble or water-insoluble compound is a compound of aluminum, zinc, chromium, cobalt, nickel, iron, tin, lead, copper, manganese, titanium, molybdenum, zirconium, bismuth, antimony or tungsten, and said compound has an average particle diameter of under 200 μ . 10
11. A method as claimed in claim 1 substantially as described herein with reference to any one of the Examples.
- 15 12. A coated steel sheet whenever obtained by a method as claimed in any of the preceding claims. 15

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